# Energy transfer at the nanoscale: diodes and pumps





Dvira Segal
 Chemical Physics Theory Group
 University of Toronto



 Nanodevices: Understand and manipulate heat transfer in molecular systems and nanoscale objects.

# Outline

#### I. Motivation

II. Models for studying the fundamentals of quantum heat flow.

#### **III. Static case: Nonlinear effects**

Thermal rectification-diode

- 1. Experiment
- 2. Formalism
- 3. Sufficient conditions for thermal rectification

#### IV. Dynamic case: Active control

Stochastic heat pumps

- 1. Mechanism
- 2. Formalism
- 3. Examples: Control of the noise properties/ solid characteristics.
- 4. Efficiency: Approaching the Carnot limit

#### V. Summary and Outlook

# Introduction/Motivation

#### **Quantum energy flow**

Vibrational heat flow Photonic heat conduction Electronic energy transfer

# Vibrational energy flow in molecules





Z. Wang, et al., Science 317, 787 (2007)

**How molecules heat up.** In the experiments reported by Dlott and coworkers, heat is transferred from the heated gold substrate along the molecular chain, causing the chain to become increasingly disordered.

Strong laser pulse gives rise to strong increase of the electronic temperature at the bottom metal surface. Energy transfers from the hot electrons to adsorbed molecule.

# Single mode heat conduction by photons



The electromagnetic power (blackbody radiation) flowing in the

device is given by: 
$$P_{\gamma} = r \int_{0}^{\infty} \omega \Big[ n_{B}^{e}(\omega) - n_{B}^{\gamma}(\omega) \Big] d\omega$$
  
coupling coefficient  $r = 4 \frac{R_{e}R_{\gamma}}{(R_{e} + R_{\gamma})^{2}}$  D. R. Schmidt et al., PRL 93, 045901  
(2004). Experiment: M. Meschke et al., Nature 444, 187 (2006).

# Exchange of information

#### Radiation of thermal voltage noise



K. Schwab Nature 444, 161 (2006)

$$G_Q = \frac{\pi^2 k_B^2 T}{3h}$$

The quantum thermal conductance is universal, independent of the nature of the material and the particles that carry the heat (electrons, phonons, photons).





 $H_{\nu}$  collection of phonons; electron-hole excitations; spins.

$$V_{v} = F_{v} \sum_{n,m} S_{n,m} |n\rangle \langle m|$$







#### III. Static Case: Nonlinear effects

$$J = \sum_{n} \alpha_{n}(T_{a}) \Delta T^{n}$$



$$\alpha_1 = \lim_{\Delta T \to 0} \quad J / \Delta T$$

Conductance

$$\alpha_2 \neq 0 \quad \rightarrow \quad \left| J(\Delta T) \right| \neq \left| J(-\Delta T) \right|$$

Thermal rectification

 $\alpha_3 < 0 \longrightarrow \partial J(\Delta T) / \partial \Delta T < 0$ 

Negative differential thermal conductance

# Harmonic model





D. Segal, A. Nitzan, P. Hanggi, JCP (2003).



# **Thermal rectification**

$$J = \sum_{n} \alpha_{n}(T_{a}) \Delta T^{n}$$

$$\alpha_2 \neq 0 \quad \rightarrow \quad \left| J(\Delta T) \right| \neq \left| J(-\Delta T) \right|$$



#### Asymmetry + Anharmonicity

Thermal Rectification

- M. Terraneo, M. Peyrard, G. Casati, PRL (2002);
- B. W. Li, L. Wang, G. Casati, PRL (2004);
- D. Segal and A. Nitzan, PRL (2005), JCP (2005).
- B. B. Hu, L. Yang, Y. Zhang, PRL (2006)
- G. Casati, C. Mejia-Monasterio, and T. Prosen, PRL (2007)
- N. Yang, N. Li, L. Wang, and B. Li, PRB (2007)
- N. Zeng and J.-S. Wang, PRB (2008)

#### **Experiment: thermal rectifier**



#### Simulations

B. W. Li, L. Wang, G. Casati, PRL (2004)



# Formalism: Master Equation

Model: 
$$H = H_S + H_L + H_R + V$$
  
 $H_S = \sum_n E_n |n\rangle \langle n|$   
 $V = V_L + V_R;$   $V_v = F_v \sum_{n,m} S_{n,m} |n\rangle \langle m|;$   $F_v = \lambda_v B_v$   
 $H_v$  collection of phonons; electron-hole excitations; spins.

Heat current: 
$$J_{\nu} = \frac{i}{2} \operatorname{Tr} \left( \left[ H_{\nu} - H_{s}, V_{\nu} \right] \rho \right)$$

Dynamics: Liouville equation in the interacation picture  

$$\frac{d\rho_{m,n}}{dt} = -i[V(t),\rho(0)]_{m,n} - \int_{0}^{t} d\tau \Big[V(t), [V(\tau),\rho(\tau)]\Big]_{m,n}$$

## Formalism: Master Equation

Liouville Equation  $\rightarrow$  Pauli Master equation

$$\dot{P}_{n}(t) = \sum_{\nu,m} \left| S_{n,m} \right|^{2} P_{m}(t) k_{m \to n}^{\nu}(T_{\nu}) - P_{n}(t) \sum_{\nu,m} \left| S_{n,m} \right|^{2} k_{n \to m}^{\nu}(T_{\nu})$$

$$k_{n\to m}^{\nu}(T_{\nu}) = \lambda_{\nu}^{2} f_{\nu}(T_{\nu}); \qquad f_{\nu}(T_{\nu}) = \int_{-\infty}^{\infty} d\tau e^{iE_{n,m}\tau} \left\langle B_{\nu}(\tau)B_{\nu}(0) \right\rangle_{T_{\nu}}$$

$$J = \frac{1}{2} \sum_{n,m} E_{m,n} \left| S_{n,m} \right|^2 P_n(t) \left[ k_{n \to m}^L(T_L) - k_{n \to m}^R(T_R) \right]$$

Weak system-bath coupling limit;  $<B\rho(0)>=0$ ; Factorization of the density matrix of the whole system; Markovian limit.

### Sufficient conditions for thermal rectification



The reservoirs have different mean energy

(2) 
$$\underbrace{\frac{n^{H}(-\omega)}{f(T_{H})} \left(\frac{1}{\lambda_{L}^{2}} - \frac{1}{\lambda_{R}^{2}}\right)}_{g(T_{H})} \neq \underbrace{\frac{n^{C}(-\omega)}{f(T_{C})} \left(\frac{1}{\lambda_{L}^{2}} - \frac{1}{\lambda_{R}^{2}}\right)}_{g(T_{C})}$$



The relaxation rates' temperature dependence should differ

from the central unit occupation function, combined with some spatial asymmetry.

$$k_{n \to m}^{\nu}(T_{\nu}) = \lambda_{\nu}^{2} f_{\nu}(T_{\nu}); \qquad f_{\nu}(T_{\nu}) = \int_{-\infty}^{\infty} d\tau e^{iE_{n,m}\tau} \left\langle B_{\nu}(\tau)B_{\nu}(0) \right\rangle_{T_{\nu}}$$

L.A. Wu and D. Segal, PRL (2009).

L.A. Wu, C.X. Yu, and D. Segal arXiv: 0905.4015

# Spin-boson thermal rectifier



# III. Dynamic Case: Active control

Until now: Heat was flowing from hot objects to cold objects.

**Question 1:** Can we direct heat against a temperature gradient?

Answer 1: Add (i) external forces (ii) asymmetry

Heat pump moves heat from a cold bath to a high temperature bath.

**Question 2:** Do we need to shape the external force in order to achieve the pumping operation?

Answer 2: Random noise can lead to pumping.





#### Simple model: Stochastic heat pump

$$H = H_{s} + H_{L} + H_{R} + V_{L} + V_{R}$$

$$H_{s} = \frac{B_{0} + \varepsilon(t)}{2} \sigma_{z}$$

$$H_{v} = \sum_{k} \omega_{k} b_{v,k}^{\dagger} b_{v,k}$$

$$V_{v} = F_{v} \sigma_{x}; \quad F_{v} = \sum_{k} \lambda_{v,k} \left( b_{v,k}^{\dagger} + b_{v,k} \right)$$

Spectral function of the reservoirs  $g_{\nu}(\omega) = 2\pi \sum_{k} \lambda_{\nu,k}^2 \delta(\omega - \omega_k)$ 

#### Mechanism: Random fluctuations catalyze heat flow



D. Segal, A. Nitzan, PRE (2006).

D Segal PRL (2008); JCP (2009).

The subsystem is coupled to both ends

The subsystem is coupled to the left side only. TLS temperature is effectively high  $T_{TLS}>T_L>T_R$ 

## Formalism: Population

Liouville equation  $\rightarrow$  Pauli Master equation

$$\left\langle \dot{P}_{1}(t) \right\rangle_{\varepsilon} = -\left(k_{1 \to 0}^{L} + k_{1 \to 0}^{R}\right) \left\langle P_{1}(t) \right\rangle_{\varepsilon} + \left(k_{0 \to 1}^{L} + k_{0 \to 1}^{R}\right) \left\langle P_{0}(t) \right\rangle_{\varepsilon}$$

Transition rates:  $k_{1\to0}^{\nu} = \int_{-\infty}^{\infty} d\omega g_{\nu}(\omega) (1 + n_{\nu}(\omega)) I(B_{0} - \omega); \qquad k_{0\to1}^{\nu} = \int_{-\infty}^{\infty} d\omega g_{\nu}(\omega) n_{\nu}(\omega) I(B_{0} - \omega)$ Spectral lineshape of the Kubo oscillator:  $I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \left\langle \exp i \int_{0}^{t} \varepsilon(t') dt' \right\rangle_{0} d\omega$ 

# Formalism: Random Frequency modulations (Kubo Oscillator)

Spectral lineshape of the Kubo oscillator:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \left\langle \exp i \int_{0}^{t} \mathcal{E}(t') dt' \right\rangle_{\varepsilon} d\omega$$
  
= exp  $K(t)$   
$$K(t) = i \int_{0}^{t} dt_{1} \left\langle \mathcal{E}(t_{1}) \right\rangle_{\varepsilon} + i^{2} \int_{0}^{t} dt_{1} \int_{0}^{t} dt_{2} \left[ \left\langle \mathcal{E}(t_{1}) \mathcal{E}(t_{2}) \right\rangle_{\varepsilon} - \left\langle \mathcal{E}(t_{1}) \right\rangle_{\varepsilon} \left\langle \mathcal{E}(t_{2}) \right\rangle_{\varepsilon} \right] + \dots$$

For a Gaussian process in the fast modulation limit  
Define 
$$\gamma \equiv \int_{0}^{\infty} dt \, \langle \mathcal{E}(t_0)\mathcal{E}(t_0 + t') \rangle$$
 Obtain:  $I(\omega) = \frac{\gamma/\pi}{\omega^2 + \gamma^2}$ 

#### Formalism: Transition rates

$$k_{1\to0}^{\nu} = \int_{-\infty}^{\infty} d\omega g_{\nu}(\omega) \left[ 1 + n_{\nu}(\omega) \right] I(B_0 - \omega) \xrightarrow{\gamma \to 0} k_{1\to0}^{\nu} = g_{\nu}(B_0) \left[ 1 + n_{\nu}(B_0) \right]$$
$$k_{0\to1}^{\nu} = \int_{-\infty}^{\infty} d\omega g_{\nu}(\omega) n_{\nu}(\omega) I(B_0 - \omega) \xrightarrow{\gamma \to 0} k_{0\to1}^{\nu} = g_{\nu}(B_0) n_{\nu}(B_0)$$

Kubo oscillator transition rates

Field-free vibrational relaxation rates

For a Gaussian process in the fast modulation limit 
$$I(\omega) = \frac{\gamma/\pi}{\omega^2 + \gamma^2}$$

# Formalism: Current

Current operator: 
$$\hat{J}_R = \frac{i}{2} [H_S(t) - H_R, V_R]$$

Master equation description:  $\langle J_R \rangle_{\varepsilon} = \langle P_1 \rangle_{\varepsilon} f_{1 \to 0}^R - \langle P_0 \rangle_{\varepsilon} f_{0 \to 1}^R$ 

$$f_{0\to1}^{\nu} = \int_{-\infty}^{\infty} d\omega \omega g_{\nu}(\omega) I(B_0 - \omega) n_{\nu}(\omega)$$
$$f_{1\to0}^{\nu} = \int_{-\infty}^{\infty} d\omega \omega g_{\nu}(\omega) I(B_0 - \omega) [n_{\nu}(\omega) + 1]$$

$$\begin{array}{l} \stackrel{\gamma \to 0}{\longrightarrow} & B_0 k_{0 \to 1}^{\nu} \\ \stackrel{\gamma \to 0}{\longrightarrow} & B_0 k_{1 \to 0}^{\nu} \end{array}$$

Kubo oscillator transition rates

Field-free vibrational relaxation rates

## Formalism: Summary

Population: 
$$\left\langle \dot{P}_{1}(t) \right\rangle_{\varepsilon} = -\left(k_{1 \to 0}^{L} + k_{1 \to 0}^{R}\right) \left\langle P_{1}(t) \right\rangle_{\varepsilon} + \left(k_{0 \to 1}^{L} + k_{0 \to 1}^{R}\right) \left\langle P_{0}(t) \right\rangle_{\varepsilon}$$

Heat current:  $\langle J_R \rangle_{\varepsilon} = \langle P_1 \rangle_{\varepsilon} f_{1 \to 0}^R - \langle P_0 \rangle_{\varepsilon} f_{0 \to 1}^R$ 

#### Transition rates:

$$k_{1\to0}^{\nu} = \int_{-\infty}^{\infty} d\omega g_{\nu}(\omega) \left(1 + n_{\nu}(\omega)\right) I(B_0 - \omega); \qquad k_{0\to1}^{\nu} = \int_{-\infty}^{\infty} d\omega g_{\nu}(\omega) n_{\nu}(\omega) I(B_0 - \omega)$$

$$f_{0\to1}^{\nu} = \int_{-\infty}^{\infty} d\omega \omega g_{\nu}(\omega) I(B_0 - \omega) n_{\nu}(\omega)$$
$$f_{1\to0}^{\nu} = \int_{-\infty}^{\infty} d\omega \omega g_{\nu}(\omega) I(B_0 - \omega) [n_{\nu}(\omega) + 1]$$





## Proof of principle for a dichotomous noise



Dichotomous noise

$$I(\omega) \sim \frac{1}{2} \Big[ \delta(\omega - \Omega) + \delta(\omega + \Omega) \Big]$$

$$g_{\nu}(\omega) = 2\pi \sum_{k} \lambda_{\nu,k}^{2} \delta(\omega - \omega_{k})$$
  
Assumption: The R Reservoir  
spectral denisty strongly varies  
within the noise spectral window  
$$g_{R}(B_{0} + \Omega) \ll g_{R}(B_{0} - \Omega)$$

If  $T_L=T_R$ , it can be shown that current is catalyzed from the R side into the L side when the following condition is satisfied

$$\frac{\left(g_{L}^{-}+g_{R}^{-}\right)n(B_{0}-\Omega)+g_{L}^{+}n(B_{0}+\Omega)}{\left(g_{L}^{-}+g_{R}^{-}\right)\left[n(B_{0}-\Omega)+1\right]+g_{L}^{+}\left[n(B_{0}+\Omega)+1\right]} < \frac{n(B_{0}-\Omega)}{n(B_{0}-\Omega)+1}$$

Or 
$$n(B_0 + \Omega) < n(B_0 - \Omega)$$

$$g_{\nu}^{\pm} = g_{\nu} (B_0 \pm \Omega)$$

#### Efficiency: Approaching the Carnot limit

Assume Einstein solids with

$$g_{\nu}(\omega) = 2\pi \lambda_{\nu}^2 \delta(\omega - \omega_{\nu})$$



$$\langle J_v \rangle_{\varepsilon} = \omega_v \mathcal{T}[n_L(\omega_L) - n_R(\omega_R)]$$

Pumping condition:  $\langle J_R \rangle < 0 \rightarrow \frac{T_L - T_R}{T_R} < \frac{\omega_L - \omega_R}{\omega_R}$ 

Work:  $\langle W \rangle_{\varepsilon} = (\omega_R - \omega_L) \mathcal{T}[n_L(\omega_L) - n_R(\omega_R)]$ 

Cooling efficiency 
$$\eta = -\frac{\langle J_R \rangle_{\varepsilon}}{\langle W \rangle_{\varepsilon}} = \frac{\omega_R}{\omega_L - \omega_R} < \frac{T_R}{T_L - T_R} = \eta_{\max}$$

### **Physical Realizations**

• Noise processes in nanomechanical resonators: Adsorption-desorption noise, temperature fluctuations.

(Clealand and Roukes, J. App. Phys., 92 2758 (2002), Y.T. Yang et al. Nano Lett (2006). ).



• The resonance frequency can be tuned by the gate- voltage fluctuations change the characteristic modes.

(Sazanova et al. Nature 431, 285 (2004).



### Exciton stochastic pump



The Metals have different band structure.

Delta-like DOS will lead to the Carnot efficiency.

Related ideas, showing reversible particle transfer, were considered in Humphrey and Linke PRL 2005.

Pumping of heat by modulating the reservoirs temperatures

Computer simulation of a heat pump where the temperature of one reservoirs is modulated periodically.



$$\begin{split} T_L(t) &:= T_L \,=\, T_0(1 + \Delta + A \cdot \operatorname{sgn}(\sin \omega t)), \\ T_R \,=\, T_0(1 - \Delta), \end{split}$$



N.Li, B. Li and P. Hanggi, EPL (2008)

Fig. 6: (Color online) Heat flux J vs. thermal bias  $\Delta$  for different driving amplitudes A = 0, 0.2, and 0.5. The lattice length is N = 50 + 50 and  $T_0 = 0.09$ . Note that the nonlinearity in the Frenkel-Kontorva part of the junction is essential to obtain the thermal ratchet effect. At large rocking strength (A = 0.5) the current bias characteristics can be manipulated to eliminate a NDTR regime at negative bias values  $\Delta$ .

# Summary

We studied quantum heat transfer in minimal models, seeking to connect the transport characteristics with the microscopic description ( $H \rightarrow J$ ?)

- Static transport: We discussed sufficient conditions for thermal rectification.
- **Dynamical control:** We studied pumping of heat due to the shaping of the reservoirs properties, given that the system is suffering a stochastic noise.

# Outlook

Formal issues:

- Going beyond the perturbative treatment.
- Add coherent effects
- Consider more realistic models.

#### Basic challenges:

- Static case: Understand other nonlinear phenomena, e.g. negative differential thermal conductance, from first principles. Understand the ballistic- diffusive heatflow crossover (Fourier law).
- Dynamic case: Control heat flow by modulating the reservoirs temperatures.

# Thanks-

#### **Rectifiers:**

Abraham Nitzan	Tel Aviv University
Lianao Wu	University of Toronto & The Basque Country University at Bilbao
Claire Yu	University of Toronto

#### Pumps:

Abraham Nitzan Tel Aviv University

#### **Thermal rectification:**

- D. Segal and A. Nitzan, PRL 94, 034301 (2005); JCP 122, 194704 (2005).
- D. Segal, PRL 100 105901 (2008).

L.A. Wu and D. Segal, PRL 102, 095503 (2009); L.A. Wu, C. X. Yu, and D. Segal arXiv 0905:4015.

#### Molecular heat pumps:

- D. Segal and A. Nitzan, PRE 73, 02609 (2005).
- D. Segal PRL 101 260601 (2008); JCP 130, 134510 (2009).

#### The rate constant is reflecting the bath properties

$$k_{n\to m}^{\nu}(T_{\nu}) = \lambda_{\nu}^{2} f_{\nu}(T_{\nu}); \qquad f_{\nu}(T_{\nu}) = \int_{-\infty}^{\infty} d\tau e^{iE_{n,m}\tau} \left\langle B_{\nu}(\tau)B_{\nu}(0) \right\rangle_{T_{\nu}}$$

Harmonic bath, bilinear coupling  $k^{\nu}(T_{\nu}) = -n_{B}^{\nu}(-\omega) \left[ 2\pi \lambda_{\nu}^{2} \sum_{j} \delta(\omega_{j} - \omega) \right]$ 

Noninteracting spinless electrons

$$n_B^{\nu}(\boldsymbol{\omega}) = [e^{\boldsymbol{\omega}/T_{\nu}} - 1]^{-1}$$

Noninteracting spin bath  $k^{\nu}(T_{\nu}) = n_{s}^{\nu}(-\omega)\Gamma_{s}^{\nu}(\omega)$ 

$$n_S^{\nu}(\boldsymbol{\omega}) = [e^{\boldsymbol{\omega}/T_{\nu}} + 1]^{-1}$$

$$n_F^{\nu}(\boldsymbol{\omega}) = [e^{(\boldsymbol{\omega}-\boldsymbol{\mu}_{\nu})/T_{\nu}} + 1]^{-1}$$

$$k^{\nu}(T_{\nu}) = n_{B}^{\nu}(-\omega) \left[ -2\pi\lambda_{\nu}^{2} \sum_{i,j} \delta(\varepsilon_{i} - \varepsilon_{j} + \omega) [n_{F}^{\nu}(\varepsilon_{i}) - n_{F}^{\nu}(\varepsilon_{i} + \omega)] \right]$$